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Japanese Patent

62167393

**FUEL ADDITIVE**  
[燃料添加剤]  
**MORITA TAKESHI et al.**

UNITED STATES PATENT AND TRADEMARK OFFICE

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## SPECIFICATION

### 1. Title of the Invention

Fuel Additive

### 2. Claims

A fuel additive which is an effective component as a composition having a fine particle surface which is comprised of one kind or 2 or more kinds of iron oxide or hydroxide with a particle diameter of 50-500Å and which has undergone absorption treatment by one kind or 2 or more kinds of naphthenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid.

### 3. Detailed Description of the Invention

(Applicable Field of the Invention)

This invention containing a high concentration of metal compounds is a fuel additive which has good solubility with crude oil which is used in combustion engines such as diesel engines, boilers, heat furnaces, gas turbines, etc., heavy oil, petroleum coke, petroleum pitch, light oil, and gasoline, etc.

(Prior Art)

Conventional fuel additives, corresponding to the purpose of their use, are known to control the occurrence of harmful components such as sulfur oxide and nitrogen oxide substances and are known to contain sludge dispersion agents, emulsion grinding agents, corrosion prevention agents, deposit prevention agent, fuel ignition promoter, smoke prevention agent, ignition promoter, solid residual reducer, and the form of these fuel additives is that of a slurry by mixing in water together with a dispersion agent whose principal component in powder form such as a non-sulfurous metal, metal oxide substance, metal hydroxide substance, and carbonate.

(Problems that the Invention is to Solve)

However, with fuel additives of this kind of form, the non-sulfurous substances which are included in the composition sometimes precipitate and separate while standing or when added to fuel oil sometimes closes up the pipe parts or burner parts and clogs the burner nozzle. Furthermore, with this kind of fuel additive, the particle diameter of the non-sulfurous substances which are included in the compositions is large, and furthermore, because the dispersion capability is poor, the contact effect with

harmful substances which exist during fuel burning is insufficient, and it is not possible to expect a sufficient effect as an additive.

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On the other hand, there are also conventional fuel additives which dissolve in petro based solution metal compounds that are oil soluble.

These fuel additives mix and dissolve uniformly with fuel oil and have good stability properties and the contact effect with harmful components which exist in the discharge gases during burning is also good, but the content of the metal components which are harmful within the oil soluble metal compounds is small, and has the shortcoming of being high priced.

Here, this invention, having a high concentration of non-sulfurous material of metal compounds and the like, has the goal of developing a fuel additive whose blending ability with fuel oils such as with crude oils which are used for diesel engines, boilers, heat furnaces, and gas turbines, and for fuel oils such as heavy oil, petroleum cokes, petroleum pitch, and gasoline.

(Means for Solving the Problems)

In order to solve the above-mentioned problems, this invention provides a fuel additive which is an effective component as a composition having a fine particle surface which is comprised of one kind or 2 or more kinds of iron oxide or hydroxide with a particle diameter of 50-500Å and which has undergone absorption treatment by one kind or 2 or more kinds of naphthenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid.

That is, this invention uses as a fuel additive a composition which absorption processes using naphthenic acid a surface of fine particles which are comprised of one kind or 2 or more kinds of iron oxide or hydroxide whose particle diameter is 50-500Å. This fuel additive is formed in the following way.

Add an alkali agent such as NaOH, KOH,  $\text{NH}_4\text{OH}$ , or  $\text{Ca}(\text{OH})_2$  to an aqueous solution of, for example, chloride salts, nitrate salts, acetates, sulfate salts, and acetate salts and after raising the pH to 9-11, add one kind or 2 or more kinds of naphthenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid, passing through the oil soluble



residuals which were generated, and with further washing with water with the goal of desalination, there is obtained a powder composition which is comprised of fine particles obtained by dehydrating through drying.

When further explaining in detail the manufacturing method of this powder composition, generally, there is generally added an alkali agent to the aqueous solution of iron oxide substance and when the pH is raised, there is produced iron hydroxide. The generated  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{FeOOH}$  have particles which accumulate, and exist as a result of the crude large particles.

In this invention the fine particles of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$ , before crude enlargement of the assembly are transformed into lipophilic particles along with preventing a crude enlargement of the particles through surface coating with naphthenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid. That is, the fine particles of  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{FeOOH}$  that were suspended in water are positively charged, and when organic materials which are non-soluble and have a negative charge are added to an

aqueous solutions of naphththenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid, lipophilic residuals are generated as before through an absorption reaction according to the plus or minus charges.

Specifically, the pH is raised to 9-11 by adding an alkali agent to the aqueous solutions of iron compounds as described above, and after generating the  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{FeOOH}$  fine particles, the solution temperature is raised to 80-85 °C, by adding organic materials such as the previously described naphththenic acid, and by heating and stirring sufficiently, with absorption on the fine particle surface of  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{FeOOH}$ , the effect is to give a fine particle surface which is lipophilic (water insoluble) and collecting residuals.

Moreover, in this instance, by adding as is naphththenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid, there may be absorption on the  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{FeOOH}$  fine particle surface, and because the powder can pass through easily, and can precipitate easily in water, when neutralized by

adding an acidic agent such as HCl at a high temperature while the fine particles are suspended in water, the generated  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{FeOOH}$  fine particles avoid becoming unstable. At this time, when adding to the suspension liquid of fine particles after dissolving by solvents such as kerosene, normal paraffin, iso-paraffin, and liquid paraffin naphthenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid, the residual collection ability of the fine particles is good, and the pass-through ability is good, and the precipitation operation in water is extremely easy, it is filter, even when no neutralized using HCl and the like. /2

Furthermore, in this instance, the drying operation for the powder after filtering becomes easy, and in addition, the disperability with respect to every kind of oil of powder is extremely easy, resulting in a uniform colloidal solution, with good stability.

The proportion of organic material to solvent is appropriate if in the range of 0.5-1:3.

The oil soluble residuals which were generated in this way are filled, and are precipitated with the goal of desalination, and furthermore, by desalination, it is

possible to obtain an iron-containing powder which is oil soluble.

The drying conditions for the powder, for example, water containing powder (water contents approximately 30%) allow making a pellet at  $\phi$  10mm or 5-10mm x 30mm, expanding on the metal and drying through heat at 1-5m/sec. In this instance, dehydration and drying are good at 95-100 °C for 30 minutes- 1 hour, and the organic material such as naphththenic acid, which is absorbing at temperatures higher than 100 °C, decomposes, and at 90 °C or less, becomes insufficient. In addition, the drying if extended to 1 hour or more is not good because such drying initiates degradation and decomposition of the organic material.

#### (Effect of the Invention)

Because the fuel additive which is related to this invention has, as an effective component, a composition which absorbs and coats a surface of fine particles which is comprised of one kind or two or more kinds of iron oxide or hydroxide materials whose particle diameter is 50-500Å such as naphththenic acid, tall oil fatty acid, petro-sulfonic acid, alkylphosphoric acid ester, oleic acid, lauric acid

and euric acid, when mixing with petroleum based solvents such as kerosene, spindle oil, liquid paraffin, light and heavy oil, plant oils such as castor oil and olive oil, high fatty acids such as olefinic acid and linoleic acid, liquid oils such as high fact acid esters like ethyl olefinic acid, squalin, and squalene, and aliphatic based solvents such as methylnaphthalene, and akylbenzene, colloidal solvents result through dispersion under conditions identical with those for dissolving.

Consequently, even adding to the fue additive a solvent which is appropriate under the same conditions for the above-mentioned composition, there is obtained uniform dispersion with the fuel oil, and consequently there is no deposition, and there is no closure of pipes or covers for the fuel oil, no abrasion.

In addition, the fuel additive which is related to this invention contains a high concentration of iron hydroxide. For example, the content rate of iron is high compared to general organic iron compounds such as petroleum iron suluphonate, iron naphthalate, and iron olefinate, with the iron being as 50-60% FeO. Furthermore, because the above-mentioned iron oxide or iron hydroxide materials are formed from fine

particles of 50-500Å, the surface area is large, physical and chemical activity is great, and the contact effect with harmful components is good. Because of this contact ability, the fuel additive which is related to this invention can be expected to have sufficient effect even with small quantities placed in the fuel oil. For example, not only is there control of the generation of smoke which contains much  $\text{SO}_x$  and  $\text{NO}_x$  which contaminates the atmosphere, it is possible to control low temperature corrosion of boilers from the generation of high temperature corrosion,  $\text{SO}_2$  and  $\text{SO}_3$  of superheating by V, Na, and S.

(Embodiments)

Below, there are shown embodiments of this invention.

Embodiment 1

A liquid	15% $\text{FeCl}_2$ aqueous solution	620 parts
B liquid	20% $\text{NH}_4\text{OH}$ aqueous solution	375 parts
C liquid	mixture of naphthalenic acid 10 parts, iso-paraffin 13 parts	

Raise to pH 9.5-10 by adding B liquid to A liquid.

After fine particles of  $\text{Fe}(\text{OH})_2$  are generated, raise the liquid temperature to 80 °C, add the C liquid, and by collecting the oil soluble powder containing iron after sufficiently heating and stirring at 80-85 °C, there results a transparent liquid.

Next, eliminate the non-sulfur salts which are contained within by filtering and precipitating. The powder which is obtained as a result of the filtering and precipitating contains water of approximately 50%, and by making a spherical pellet of phi 10mm, expand in a wire net of 200 mesh, reduce the water content to 2.1% by hot air drying for 40 minutes at 95 °C with wind velocity at approximately 3m/sec.

Add to the same weight mixture of A heavy oil and alkyl benzene after drying, and perform stirring and mixing using a [UNKNOWN], to obtain a 40% (wt. %) dispersed liquid.



## Embodiment 2

A liquid	15% $\text{FeCl}_2$ aqueous solution	300 parts
B liquid	20% KOH aqueous solution	150 parts
C liquid	a mixture solvent of tall oil fatty acid and 4 parts and kerosene 8 parts	

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Add B liquid to A liquid, raise the pH to 9.5-10, and after fine particles of  $\text{Fe}(\text{OH})_3$  are generated, raise the liquid temperature to 80 °C and add C liquid, and perform sufficient heating and stirring at 80-85 °C to give an oil soluble powder which contains barium, becoming transparent.

Next, perform filtering and precipitation. The powder which is obtained after filtering and precipitation contains 50% water, and expand to a metal net of 300 mesh by making a pellet in the form of a rectangular solid of 5mm x 10mm x 30mm, and dry for 30 minutes with hot air at , air velocity 5m/sec and temperature 95 °C. Powder is obtained with 3% content. Disperse in lamp oil by [UNKNOWN] the powder after drying to obtain a 50% (wt.%) dispersed liquid.

## Embodiment 3

A liquid	15% $\text{FeCl}_2$ aqueous solution	350 parts
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B liquid	20% $\text{NH}_4\text{OH}$ aqueous solution	200 parts
C liquid	mixture solvent liquid of petroleum sulphonic acid 8 parts and kerosene 8 parts	

Add B liquid to A liquid, and along with raising the pH to 9.5-10, oxidize  $\text{FeCl}_2$  by blowing air and after generating fine particles of  $\text{FeOOH}$ , raise the liquid temperature to 80 °C, add C liquid, and perform sufficient heating and stirring at 80-85 °C, and by collecting the oil soluble powder which contains iron, a liquid is produced which is transparent.

Next, eliminate the non-sulfur salts which are contained by filtering and precipitating. The powder which is obtained by filtering and water precipitation has 60% water, and make the powder in a spherical pellet of phi 10mm, expand in a metal net of 200 mesh, perform drying by passing through hot air for one hour at 90 °C with the air velocity at 1m/sec to give a powder with water contents 2%.

Add the powder after drying to alkyl benzene and obtain a dispersed liquid of 40% 4 parts by stirring and mixing by [UNKNOWN].

Application Example

By mixing every liquid which was obtained by manufacturing methods 1, 2, and 3, strongly controlled in a fuel pipe of a boiler by allocating 1 part in 1000 parts of fuel oil by utilizing a plunger pump, along with the fuel, jet to the center of the fire in the boiler and measure the amounts of [UNKNOWN] which is generated at the boiler's air heater's outlet,  $\text{SO}_2$ , and amount of catalyst(?), measure the  $\text{SO}_3$  at the outlet of the economizer, and in addition, and suspending the superheater (JIS G3462 material STBA-24) and the test piece on the air heater (JIS G3101 material SS-41), and by measuring the corrosion amount compare with respectively with non-additives. The results are shown below.

Moreover, the utilized boiler is a Mitsubishi CE self fuel circulating type, whose maximum continuous evaporation amount is 350T/H, maximum utilized pressure  $125\text{Kg/cm}^2$ , maximum utilized temperature  $540\text{ }^\circ\text{C}$ , and maximum fuel utilized 21.3Kg/H.

	nitrous oxide		SO <sub>2</sub>		SO <sub>3</sub>		Cataly
	measured value	control rate %	measured value	control rate %	measured value	control rate %	measur value
M1	230	18	806	35	30	34	98
M2	241	14	905	27	35	22	86
M3	232	17	843	32	34	25	96
Non- additive	280		1240		45		130

M1, M2, and M3 are manufacturing examples 1, 2, and 3 respectively.

Provided that the measured amounts are for NO<sub>x</sub>, SO<sub>2</sub>, and SO<sub>3</sub>, the catalyst is all ppm, and the test piece corrosion amount is mdd (mg/dm<sup>2</sup>/day)

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Written Amendment (Voluntary)

To: JPO Kuroda

# 1. Disclosure of Matter

S61-8920

## 2. Title of the Invention

Fuel Additive

3. Person making amendment

Relationship with matter    Applicant

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5. Subject of amendment

Item of "Detailed Description of the Invention" in  
Specification

5. Details of amendment

Details

1) Correct in specification the following items of

"Detailed Description of the Invention"

a) Change "dispensar" to dispenser" on p.10 line 17

b) Change "barium contents" to "iron contents" on  
p.11 line 7

c) Change "21.3Kg/H" to "21.3Kl/H" on p.13 line 9.

End

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MASAKI  
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(54) FUEL ADDITIVE

(57) Abstract:

PURPOSE: An additive having an inorganic substance such as metallic compound, etc., and improved compatibility with fuel oil, containing a composition as an active ingredient obtained by subjecting the surface of fine particles of iron oxide(hydroxide) to adsorption treatment with a specific compound.

CONSTITUTION: The aimed fuel additive comprising a composition as an active ingredient obtained by subjecting

the surface of fine particles comprising one or more of iron oxide(hydroxide) having 50W500&angst; particle diameter to adsorption treatment with one or more of naphthenic acid, tall oil fatty acid, alkylphosphoric acid ester, oleic acid, lauric acid and euric acid.

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#### LEGAL STATUS

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